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INTERACTION OF SOLUTES WITH STRETCHED POLYMERS(U) UTAH
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FEB 85 ARO-18621. 11-CH DRAG29-82-K-0024

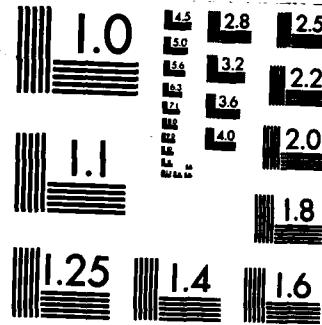
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AD-A154 662

FINAL TECHNICAL REPORT ON USARO CONTRACT "Interaction of Solutes with
Stretched Polymers", DAAG 29-82-K0024, December 15, 1981 - March 15, 1985

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February 25, 1985

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM																		
1. REPORT NUMBER ARO 18621.11-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A																		
4. TITLE (and Subtitle) Interaction of Solutes with Stretched Polymers		5. TYPE OF REPORT & PERIOD COVERED 14 Dec 81 - 13 Dec 85 Final Report																		
7. AUTHOR(s) Josef Michl Paul J. Phillips		6. PERFORMING ORG. REPORT NUMBER N/A																		
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Utah Salt Lake City, Utah		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A																		
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park NC 27709		12. REPORT DATE Feb 85																		
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 10																		
		15. SECURITY CLASS. (of this report) Unclassified																		
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE																		
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)																				
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Solutes, Crystallization, Polymers, Molecular Structure, Solvents, Polyethylene).																				
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Significant advances have been made in the understanding of polymer-solute interactions and in the understanding of solute properties. This report pertains to: 85 5 06 230																				

This three-year project has resulted in 10 publications in refereed journals, one Ph.D. dissertation, and one nearly complete M.S. thesis. Several additional papers are under preparation and will be submitted to the agency as they appear.

Appendix I contains a list of all the papers published and the copies of these publications. Since the papers describe the results in detail, we believe that there is no need to repeat the information here. The following text is therefore restricted to highlighting the main accomplishments.

Cont'd → Dielectric relaxation studies -

→ Solute molecules containing dipole moments have been used in order to obtain information on the location of molecules in polyethylene. Several different types of oriented polyethylene were used including drawn film, extruded rod and single crystal texture material produced by slit extrusion and high-pressure annealing. Each polymer type was studied in the undoped state first. Studies showed, at a very early stage, that the α -loss process known to be associated with internal motions of the crystalline phase was totally unaffected by the presence of dipolar solutes. This result demonstrated clearly that proposed mechanisms of orientation involving the solute entering into the polyethylene crystals were not valid. All possible orientation mechanisms were reviewed leading to the conclusion that oriented adsorption of solute molecules on the surfaces of microfibrillar crystals was the most likely mechanism.

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Major dielectric-relaxation peaks were observed at low temperatures. Two peaks were often noted, one in the vicinity of the γ -loss process of polyethylene and a lower temperature peak labelled δ . Both peaks are related

to the individual motion of the molecules, the δ peak reflecting a relatively immobile state below the glass temperature of the polymer and hence indicating the motion of the molecule within its 'cage'. The γ -process occurs when the molecules become liberated due to the onset of polymer chain mobility at the glass transition. The temperature location of both peaks depends on molecular size showing that the onset of mobility in the polymer chains is a gradual process successively larger sections being able to cooperately rearrange as temperature is increased.

Quantitative analyses of peak intensities showed that only a fraction of the solute molecules were liberated during these processes. Therefore either molecules were immobilized through some form of strong adsorption or were located on sites in which orientation by the electric field was impossible. Studies of oriented rod specimens in which experiments could be carried out both parallel and perpendicular to the orientation direction were expected to resolve the problems. Experimentation is complete but analysis is still underway. The fraction of 'lost' molecules is greater for oriented film compared to unoriented film and also for the better oriented molecules. Studies on solutes in single crystal texture polyethylene showed almost total immobilization of orientable solutes.

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DSC and spectroscopic studies -

→ FTIR and polarized UV spectroscopic studies have been enlightening for acridine in polyethylene. UV studies showed the presence of microcrystals in oriented film at relatively low concentrations but of isolated molecules in unoriented film at even high concentrations. Differential scanning

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calorimetry has demonstrated the presence of microcrystals of acridine also, in both stretched sheets and extruded rod samples. The oriented microcrystals of acridine are likely to have grown epitaxially on the surfaces of polyethylene microcrystals produced by drawing. It is known that polyethylene and anthracene are epitaxially compatible and studies of the growth of polyethylene on anthracene have now been reported in the literature. Current studies are aimed at showing that acridine can epitaxially crystallize on specially grown films of polyethylene having the (110) crystal faces exposed. It now seems clear that the orienting mechanism, in the case of well oriented solute molecules, is epitaxial crystallization on the exposed (110) faces of polyethylene microfibrillar crystals.

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→ Electron microscopic studies:

A good test of the adsorption/epitaxial crystallization processes would be to vary the diameter of the microfibrils. Such a procedure would result in a change in the (110) surface area per unit volume sample and hence a change in the fraction of molecules oriented for a given concentration. Since it is not known how to alter the microfibrillar diameter, morphological studies of the drawing process have been carried out for specimens of initially different morphologies. Permanganic etching followed by surface replication and transmission electron microscopy proved to be a powerful technique producing very detailed information on the transformation process not previously available. We have recently shown that the microfibrillar size can be changed by varying the initial crystallization temperature but have not yet been able to carry out the necessary spectroscopic studies mentioned at the beginning of this section.

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Transmission electron microscopic studies of oriented thin films have also been carried out. It proved impossible to see acridine crystals inside the film but studies of crystals grown epitaxially on the film surfaces could be carried out.

More studies are needed for additional solute molecules in order to learn the extent of applicability of the epitaxial mechanism. However, studies of a molecule of similar size to acridine which would have difficulty in crystallizing epitaxially, 9-bromoanthracene, show that it cannot be oriented nearly as efficiently by stretched polyethylene.

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Solute orientation factors from spectral measurements -

The orientation distribution functions of solutes in uniaxially stretched polyethylene can be characterized by their moments. The second moments of this function have been obtained from measurements of uv linear dichroism for over a hundred aromatic molecules and independently from measurement of linear ir dichroism for well over 50 aromatic and non-aromatic molecules ranging from molecules as small as triatomics to molecules as large as tricyclic aromatics, such as acridine. Both the second and the fourth moments of the orientation distribution function were obtained for four aromatic molecules by combining measurements of linear dichroism in the uv and ir with fluorescence studies in the uv and visible regions. 2-Fluoropyrene has thus become the first molecule for which all five independent second and fourth transition moments have been determined in a uniaxial medium of any kind.

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From these results a considerable amount of information on structure-orientation relationships was derived. These were further supported by computer simulations using empirical intermolecular interaction potentials.

The comparison of second and fourth moments demonstrated that the orientation distribution function of the larger aromatics peaks sharply about the most probable orientation. This is compatible with the notion that the bulk of the solid molecules present in stretched polyethylene are present in well-defined orientations located on the faces of the microcrystalline regions.

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Dynamic aspects of orientation

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A time-resolved polarized spectrofluorimeter was constructed and put into operation. In recent months results have been obtained on the motion of 2-fluoropyrene in stretched polyethylene as a function of temperature. So far only the limiting cases of essentially no motion or very fast motion on the nanosecond time scale of the instrument have been investigated. The latest experiments are aimed at investigation of motion at temperatures at around -60° C, believed to be appropriately matched to the ~ 200 ns fluorescence lifetime of the molecule. A detailed analysis will be possible only after the results are collected.

In a very different regime of much lower temperatures and much slower motions we have investigated both the rotational and the translational diffusion of the solid molecules by ir linear dichroism spectroscopy. The rotational ability of low-symmetry molecules was clearly seen to be anisotropic. For a spherical molecule of the size of adamantane rotation in stretched polyethylene becomes rapid on the time scale of seconds at about 140 K. Translational diffusion was followed by the dimerization of a reactive intermediate produced photochemically at low temperature. The dimerization rates, believed to be diffusion controlled, were a sensitive function of

solute size and a detailed research program for a systematic investigation of both rotational and translation mobility in stretched and isotropic polymer materials has been proposed.

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Solute conformations:

It has been possible to utilize measurements of ir linear dichroism to study molecular conformations in several instances. These were biphenyl, which was found to be planar in stretched polyethylene, while 4,4'-dibromobiphenyl is twisted, progesterone, for which the conformation of the acetyl group was determined, and triphenylene which was shown to be slightly nonplanar. Results such as these are of considerable interest for the understanding of shapes and activity of organic molecules.

→ Spectroscopy. Origination Supplied Keywords include:

Assignments of vibrational symmetries have been made for a large number of transition in a series of molecules ranging from triatomics to large aromatics, based on linear dichroism in the ir region. The method for these determinations has been developed to considerable degree and it is now possible to perform such measurements rapidly and reliably. This represents a significant advance in the analysis of molecular vibrations, particularly for large molecules which cannot be conveniently studied in the gas phase. As a part of this investigation the first direct polarization direction of an ir transition of a metastable state of an aromatic (acridine) has been performed.

In addition it was discovered that the molecular environment, even in non-polar media, can have a very large effect on the uv transition moment directions for weak transitions. This was demonstrated reliably both by

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measurements in stretched polyethylene and in a glassy organic solvent, 3-methylpentane. The significance of these results is severalfold. First, they account for the repeated failure to reach theoretical polarization ratio values in photoselection experiments performed in many laboratories over the last few decades on molecules with such weak transitions, such as many aromatics. Second, although the ease with which the weak transition moments are twisted is a nuisance when it comes to symmetry assignments of electronic transitions, it can conversely be viewed as an extremely sensitive probe for solute - solvent interactions, to be exploited in the future. Finally, third, the discovery served as an important warning signal for work using molecules such as pyrene derivatives as environmental probes in membranes, micelles, etc., since the dynamic measurements of their motion by the time-resolved fluorescence polarization technique will be distorted by the effects due to the solvent-induced transition moment twisting.

Summary

In conclusion, significant advances resulted from this work, both in the understanding of polymer-solute interactions and in the understanding of solute properties.

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